Kinetics and mechanism of pyruvic acid degradation by ozone in the presence of PdO/CeO$_2$

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ABSTRACT

This work investigated the catalytic ozonation of pyruvic acid (PA) in the presence of PdO/CeO$_2$ (i.e., Pd deposited on CeO$_2$) with focus on the kinetics of PA degradation at different catalyst dosages, reaction pHs and temperatures, as well as the possible catalytic mechanism. By analyzing the kinetic contributions of heterogeneous and homogeneous reactions to PA degradation, it was found that the presence of PdO/CeO$_2$ significantly enhanced the degradation of PA compared to ozonation alone especially at acidic pHs (3.0–6.0). The catalytic degradation of PA took place on the catalyst surface, which was irrelevant to hydroxyl radicals in the bulk solution. Temperature exhibited an insignificant effect on PA degradation in the range of 12–32 °C. Synergic effect was observed between PdO and CeO$_2$ on aqueous ozone decomposition, catalytic ozonation, and adsorption of PA with PdO/CeO$_2$. Ozone and PA were first adsorbed and then activated by the active sites on catalyst surface, and thus becoming more reactive to each other. The influence of phosphate on catalytic ozonation of PA corroborated that the adsorption of PA onto PdO/CeO$_2$ was a critical step for the overall reaction. ATR-FTIR analysis showed that PdO/CeO$_2$ possessed more Lewis acid sites than CeO$_2$, and Pd tended to be the main active sites. Neither •OH nor O$_2$•$^-$ was involved in the catalytic ozonation of PA as respectively substantiated by the experiments with *t*-BuOH (as •OH scavenger) and nitro blue tetrazolium (as O$_2$•$^-$ indicator).

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1. Introduction

Heterogeneous catalytic ozonation, which can be conducted under ambient conditions and may be easily applied in real water treatment without any auxiliary thermal or light systems, has received increasing research interests in recent years especially for the removal of refractory organic pollutants from water [1–3]. The catalysts commonly used in the heterogeneous catalytic ozonation were focused on activated carbon [4,5], and transition metal oxides (e.g., Fe$_2$O$_3$ [6], TiO$_2$ [7], MnO$_2$ [8]) or supported metal/metal oxides (e.g., Ru/CeO$_2$ [9], Co/Al$_2$O$_3$ [10], Cu/Al$_2$O$_3$ [11]). Pyruvic acid (PA), a major by-product formed during ozonation of water containing dissolved aromatic compounds or natural organic matter, can hardly be further oxidized by ozone ($k = 0.025$ min^{-1}) [12]. Some metal oxides (or supported metal oxides) have thus been developed to improve PA degradation in ozonation [6–11,13]. However, most of these works were conducted at rather low pHs, which was unfavorable for the practical application of catalysts. For example, a high removal of PA was achieved at pH 2.5 in catalytic ozonation with Co/Al$_2$O$_3$ [10] and at pH 2.0 with perovskite (LaTi$_{0.15}$Cu$_{0.85}$O$_3$) [13].

CeO$_2$ has been extensively studied and applied in heterogeneous catalysis because of its ability to absorb and release oxygen through a fast Ce^{3+}/Ce^{4+} cycle [14]. Meanwhile, Pd is generally used to catalyze the decomposition of gaseous organic compounds by oxygen [15]. In our previous work [16], it was found that PdO/CeO$_2$ (i.e., PdO deposited on CeO$_2$) could obviously promote PA degradation at pH below 7.4 and exhibited a persistently high activity in the semi-continuous catalytic ozonation. Pd loading onto CeO$_2$ changed the surface properties of the support material, such as pH$_{pzc}$, surface charging and the valence distribution of the constituted metal elements. This change resulted from the electron-transfers between Ce and Pd, which was supported by the XPS (X-ray photoelectron spectroscopy) analysis.

This work was to investigate the catalytic effect of PdO/CeO$_2$ on the kinetics of PA degradation by ozone under different reaction conditions. Moreover, based on the detailed study about the subtle interactions among PdO/CeO$_2$, ozone and PA, a possible surface catalysis mechanism was proposed.

2. Experimental

2.1. Catalyst preparation

CeO$_2$ was synthesized through a urea-hydrothermal route described by Xu with minor modification [17]. Specifically,

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Ce(NO$_3$)$_2$·6H$_2$O and urea were co-dissolved in distilled water with a molar ratio of 1:3, transferred to a sealed stainless steel vessel and heated at 140 °C for 5 h. After filtration and repeated washings, the precipitate was dried at 120 °C for 2 h and then calcined at 450 °C for 4 h.

PdO/CeO$_2$ was prepared by impregnating CeO$_2$ with Pd(NO$_3$)$_2$ aqueous solution following the incipient wetness impregnation method [18]. The mixture was dried at 60 °C and then calcined in air at 400 °C for 3 h. The prepared PdO/CeO$_2$ particles had an average BET surface area of 89.6 m^2 g^{-1} and an average diameter of 9.8 μm.

2.2. Experimental procedure

PA ozonation experiments were carried out in a magnetically stirred glass reactor (1.0 L) equipped with ports for ozone gas introduction and sample withdrawal. Borate buffer (10 mM) was used in pH adjustment from 6.0 to 8.8, and diluted HCl and boric acid was responsible for the pH below 6.0. The reaction temperature was controlled with water bath. Ozone gas, generated from dried oxygen with an ozone generator (3S-A5, Tonglin Technology, Beijing), was continuously bubbled into the reactor. The flow rate of ozone gas was kept constant at 4 L min^{-1} and the gaseous ozone concentration was adjusted by changing the electric current of the ozone generator. Samples withdrawn at specific time intervals were immediately filtered with 0.45 μm fibber filters before analysis. Gaseous and aqueous ozone concentrations were determined with an iodimetric method and an indigo method, respectively [19,20]. The concentration of PA was analyzed on a high-performance liquid chromatograph (HPLC, 1200 Agilent) equipped with an Atlantis dC18 column and a UV detector at 215 nm. The mobile phase (0.8 mL min^{-1}) was a mixture of 10 mM NaH$_2$PO$_4$ solution (pH 2.8, adjusted by H$_3$PO$_4$) and methanol (V/V = 95/5). The optical characteristics of the filtered samples were obtained on a UV–vis spectrophotometer (Hach DR 5000) from 350 to 800 nm. In situ ATR-FTIR spectroscopy was conducted as described by Lv et al. [21].

3. Results and discussion

3.1. Kinetics of PA degradation

3.1.1. Influence of catalyst dosage

As manifested in Fig. 1A, PA degradation in catalytic ozonation with PdO/CeO$_2$ followed an apparent first reaction order, and the apparent rate constant increased from 0.0025 to 0.016 s^{-1} as the PdO/CeO$_2$ dosage was raised from 50 to 500 mg L^{-1}. This could be related to the increase of surface active sites for PA, ozone, and radical interactions with the increased PdO/CeO$_2$ dosage.

PA degradation may occur on the catalyst surface (i.e., heterogeneous reaction) and/or in the bulk solution (i.e., homogeneous reaction). A simplified kinetic model [22] that considered the contributions from both homogeneous and heterogeneous reactions was used to describe PA degradation in catalytic ozonation:

$$-\frac{dC_{PA}}{dt} = r^{PA}_{hom} + r^{PA}_{het} = (k^{PA}_{hom} + k^{PA}_{het}C_{Pd-Ce})C_{PA} = k^{PA}_{glob}C_{PA} \quad (1)$$

where r^{PA}_{hom} and r^{PA}_{het} are the degradation rates of PA in the homogeneous and heterogeneous reactions, respectively; k^{PA}_{hom} and k^{PA}_{het} are the corresponding rate constants; k^{PA}_{glob} represents the apparent first-order rate constant of the global reaction; and C_{Pd-Ce} represents the surface density of active sites of PdO/CeO$_2$.

The values of k^{PA}_{glob} at different catalyst dosages were equal to the linear slopes in Fig. 1A, which were further plotted as a function of PdO/CeO$_2$ dosages (Fig. 1B, red line). The linear slope in Fig. 1B denotes the apparent second-order rate constant of PA degradation due to heterogeneous reactions
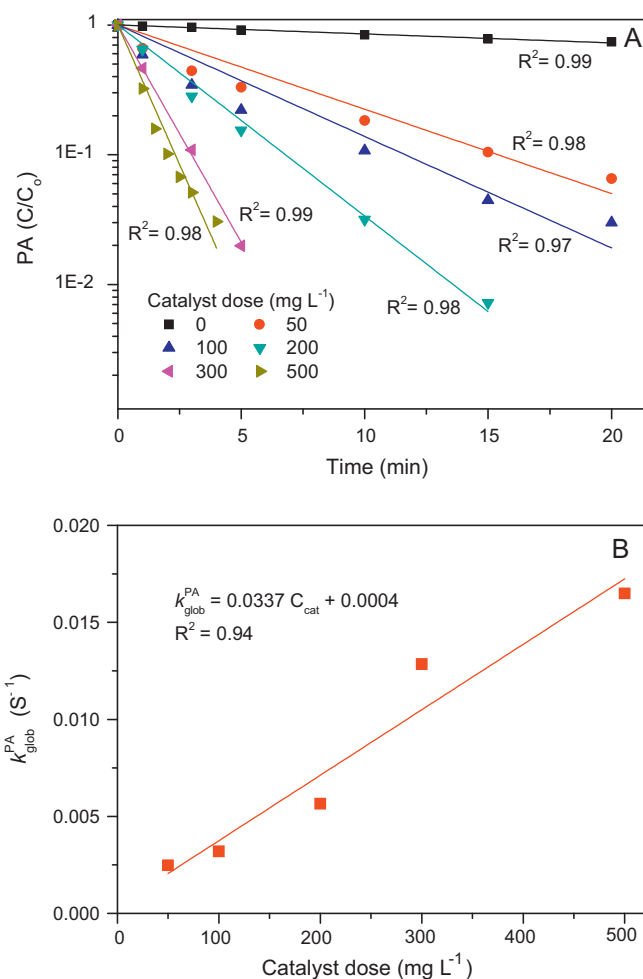

Fig. 1. Kinetics of PA degradation in catalytic ozonation with PdO/CeO$_2$ at different dosages: (A) effect of catalyst dosage on PA degradation rate; and (B) variation of the apparent first-order constant of PA global reaction (k^{PA}_{glob}) as a function of PdO/CeO$_2$ dosage. Experimental conditions: [PA]$_0$ = 5.0 ± 0.5 mg L^{-1}, C$_{O_3,gas}$ = 1.4 mg L^{-1}, pH 4.7, T = 22 °C.

(i.e., k^{PA}_{het} = 337.0 × 10^{-4} g^{-1} L s^{-1}), and the intercept denotes the apparent first-order rate constant of homogeneous reactions (i.e., k^{PA}_{hom} = 4.0 × 10^{-4} s^{-1}) with a correlation coefficient (R^2) of 0.94. Moreover, $k^{PA}_{O_3}$ (2.6 × 10^{-4} s^{-1}, Fig. 1A) was somewhat lower than k^{PA}_{hom} (4.0 × 10^{-4} s^{-1}), which was possibly due to the homogeneous catalysis caused by the leached metals from the catalyst. It was noticed that the concentrations of Ce and Pd leached from the catalyst increased as the catalyst dosage was increased, with the maximum and minimum concentrations being 38.5 (Ce), 1.87 (Pd) and 13.2 (Ce), 0.97 (Pd) μg L^{-1} after 20 min of reaction, respectively. However, the leached amounts only accounted for less than 0.5% of the corresponding metals of the catalyst.

The contribution of radical oxidation reactions to the overall PA removal can be expressed as follows [22,23]:

$$\delta^{\bullet OH} = 1 - \left(\frac{k^{PA}_{obs}}{k^{PA}_{glob}}\right) \quad (2)$$

where k^{PA}_{obs} and k^{PA}_{glob} represent the apparent first-order rate constants in the presence and absence of *tert*-butyl alcohol (*t*-BuOH), respectively, under the same pH condition. However, after the addition of *t*-BuOH into the catalytic ozonation of PA with PdO/CeO$_2$ (pH 4.7), it was found that k^{PA}_{obs} did not decrease but slightly increased (Fig. 2). The value of $\delta^{\bullet OH}$ was thus less than zero, implying that
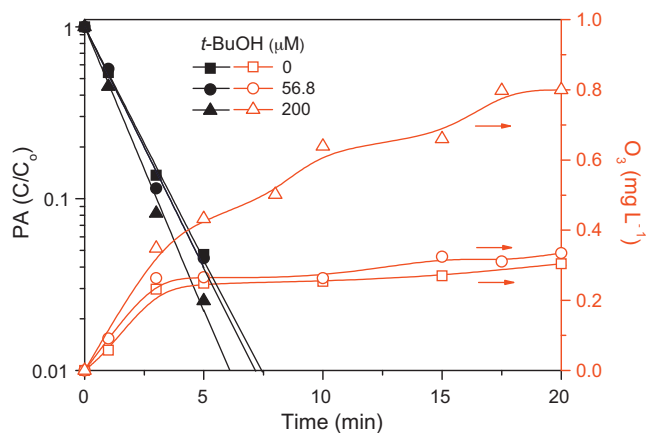
Fig. 2. Effect of t-BuOH on PA degradation and aqueous ozone concentration in catalytic ozonation. Experimental conditions: $[PA]_o = 5.0 \pm 0.5$ mg L^{-1}, $C_{O_3,gas} = 1.4$ mg L^{-1}, pH 4.7, $T = 22\,^\circ$C, catalyst dosage = 300 mg L^{-1}, $[t\text{-BuOH}] = 4.2$ mg L^{-1}.

the aqueous radicals were not involved in the catalytic ozonation of PA. The positive effect of a free radical scavenger suggests that the reactions should predominantly take place on the catalyst surface [13]. The addition of t-BuOH inhibited the decomposition of ozone to $^\bullet$OH in the bulk solution, thus rendering more ozone to be adsorbed by or react with the active sites of the catalyst, which was confirmed by the increased aqueous ozone concentration in the presence of t-BuOH (Fig. 2).

It is seen that PA degradation in the catalytic ozonation with PdO/CeO$_2$ was predominantly due to the heterogeneous catalysis on catalyst surface.

3.1.2. Influence of reaction temperature

Fig. 3 shows the influence of reaction temperature on the catalytic ozonation of PA in the range of 12–32 °C. It is known that a low temperature favors the solubilization of ozone [24]. On the other hand, increasing the temperature usually raises the reaction rate. Actually, the aqueous ozone concentration gradually decreased from 1.1 mg L^{-1} at 12 °C to 0.8 mg L^{-1} at 32 °C (data not shown). Meanwhile, the adsorption of PA onto PdO/CeO$_2$ kept nearly the same at different temperatures examined (Fig. 3). The overall result was that the variation of temperature did not notably affect the removal of PA (Fig. 3). The degradation rate constants of PA were
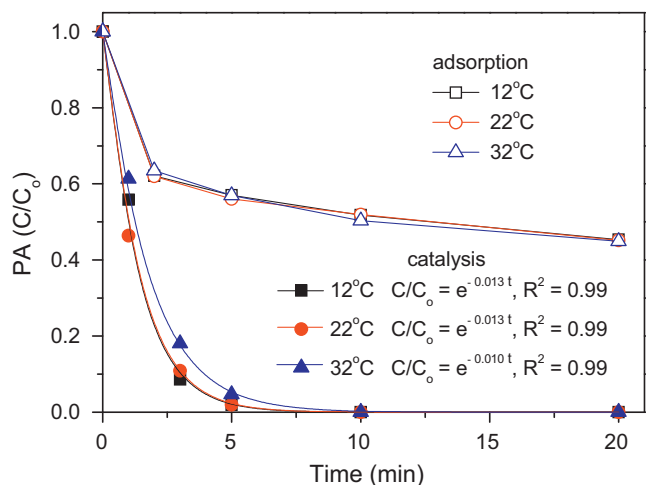

Fig. 3. Effect of reaction temperature on PA degradation and adsorption with PdO/CeO$_2$. Experimental conditions: $[PA]_o = 5.0 \pm 0.5$ mg L^{-1}, $C_{O_3,gas} = 1.4$ mg L^{-1}, pH 4.7, catalyst dosage = 300 mg L^{-1}.

Table 1
Apparent first-order rate constants of PA degradation ($k_{glob}^{PA} \times 10^4$ s^{-1}) in ozonation and catalytic ozonation at different pHs.

pH	3.0	4.7	6.0	7.4	8.8
Ozonation	9.5	2.6	0.7	0.6	2.4
Catalytic ozonation	459.6	366.2	128.6	5.3	2.0
δ^{het} (%)	97.9	99.3	99.4	89.5	−21.8

$\delta^{het} \leq 0$ means no contribution from heterogeneous reaction.

determined to be 0.013, 0.013 and 0.010 s^{-1} at 12, 22 and 32 °C, respectively.

3.1.3. Influence of pH

The apparent first-order rate constants of PA degradation ($[PA]_o = 5.0$ mg L^{-1}) at different pHs in ozonation and catalytic ozonation are compared in Table 1. The result revealed that PA degradation rate in ozonation was increased by about 15 times as pH decreased from 7.4 to 3.0, indicating that PA oxidation would be more related to molecular ozone at acidic pHs. In addition, PA degradation rate also increased when the pH increased from 7.4 to 8.8, which was probably ascribed to the generation of $^\bullet$OH from aqueous ozone decomposition at alkaline pHs. In contrast, the PA degradation rate in catalytic ozonation significantly increased by 230 times as pH decreased from 8.8 to 3.0, implying that the catalytic mechanism was not related to aqueous $^\bullet$OH. This also agreed with the positive effect of t-BuOH on PA degradation.

To estimate the kinetic contribution of heterogeneous reactions to PA degradation, δ^{het} was used and defined as follows [23]:

$$\delta^{het} = \frac{k_{glob}^{PA} - k_{O_3}^{PA}}{k_{glob}^{PA}}. \tag{3}$$

The values of δ^{het} (Table 1) clearly showed that PA degradation mainly occurred on the surface of PdO/CeO$_2$ at pH $\leq$ 7.4, but mainly occurred in the bulk solution at pH 8.8. The surface reaction seemed to occur between the adsorbed PA and ozone (or intermediate oxidants produced from ozone decomposition). The bulk reaction was mainly due to the direct molecular ozone oxidation at acidic pHs and the indirect hydroxyl radical oxidation at alkaline pHs. In the pH range of 3.0–7.4, more than 90% of PA was degraded through heterogeneous reactions.

3.2. Proposed mechanism

3.2.1. Synergic effect between PdO and CeO$_2$

Fig. 4 shows the PA removal rate in catalytic ozonation with CeO$_2$, PdO and PdO/CeO$_2$ individually. CeO$_2$ and PdO were dosed at an equivalent amount of Ce or Pd as that contained in PdO/CeO$_2$. The result showed that the PA removal rate in the catalytic ozonation with either CeO$_2$ or PdO was much lower than that with PdO/CeO$_2$. The unit activity of PdO was higher than that of CeO$_2$ since 12 mg L^{-1} PdO led to a similar PA removal as 288 mg L^{-1} CeO$_2$. Therefore, Pd seemed to be the active site on the catalyst. In comparison, PA was completely degraded at 10 min in the catalytic ozonation with PdO/CeO$_2$, which was much higher than the total removal achieved by the two metal oxides. Therefore, a synergic effect between PdO and CeO$_2$ in PdO/CeO$_2$ should exist in the catalytic reaction. In addition, PA removal in catalytic ozonation with PdO/CeO$_2$ was obviously higher than that in adsorption alone, indicating that PA was mainly removed by oxidation instead of adsorption. It was also noted that PdO/CeO$_2$ exhibited a higher adsorption capacity for PA than CeO$_2$, PdO and even their summation, implying that the synergetic effect was also responsible for PA adsorption.
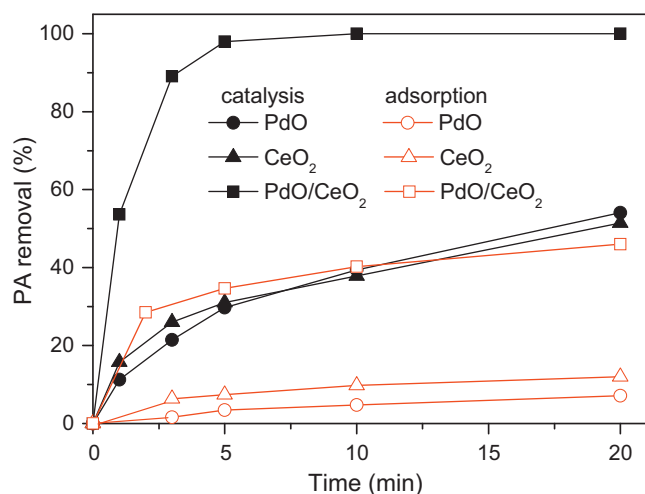
Fig. 4. Catalytic ozonation and adsorption of PA with CeO_2, PdO and PdO/CeO_2. Experimental conditions: $[PA]_o = 5.0 \pm 0.5$ mg L^{-1}, $C_{O_3,gas} = 1.4$ mg L^{-1}, pH 4.7, $T = 22\,°C$, catalyst dosage: $PdO/CeO_2 = 300$ mg L^{-1}, $CeO_2 = 288$ mg L^{-1}, PdO = 12 mg L^{-1}.

3.2.2. Ozone decomposition

In the semi-continuous reaction mode (pH 4.7, without PA), the presence of CeO_2 did not promote but slightly inhibited aqueous ozone decomposition (Fig. 5). On the contrary, the presence of PdO/CeO_2 significantly reduced aqueous ozone concentration (over 80% in the first 10 min), indicating that the supported PdO was active in promoting ozone decomposition. However, PdO alone was much less efficient than PdO/CeO_2 in promoting ozone decomposition. Therefore, a synergic effect also existed between PdO and CeO_2 on aqueous ozone decomposition. Since CeO_2 did not promote ozone decomposition, PdO should have been activated by its support material, CeO_2. On the other hand, t-BuOH addition did not obviously inhibit ozone decomposition in catalytic ozonation with PdO/CeO_2 because ozone concentration was still much lower than that in ozonation alone. Therefore, the aqueous ozone decomposition in the presence of PdO/CeO_2 was a surface catalytic process.

As discussed in the above Section 3.1.1, the homogeneous reaction with •OH had negligible effect on the catalytic degradation of PA. Additionally, since PA degradation in ozonation alone was enhanced at acidic pHs, molecular ozone seemed to be responsible
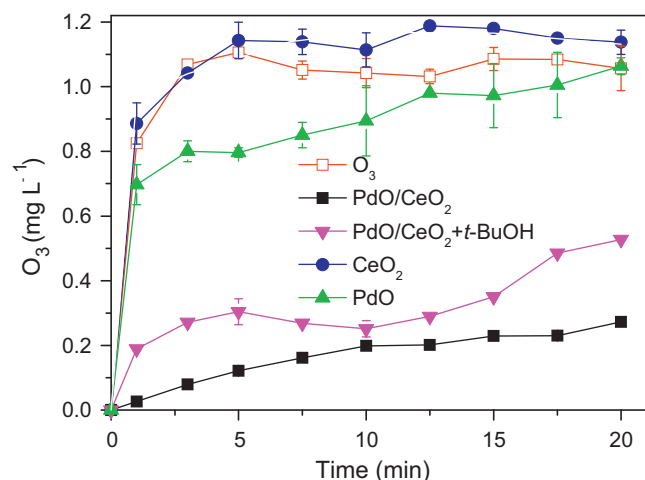

Fig. 5. Influence of catalysts on aqueous ozone concentration in semi-continuous reactions. Experimental conditions: $C_{O_3,gas} = 1.4$ mg L^{-1}, pH 6.0, $T = 22\,°C$, $[t$-BuOH$] = 56.8\,\mu M$, catalyst dosage: $PdO/CeO_2 = 300$ mg L^{-1}, $CeO_2 = 288$ mg L^{-1}, PdO = 12 mg L^{-1}.

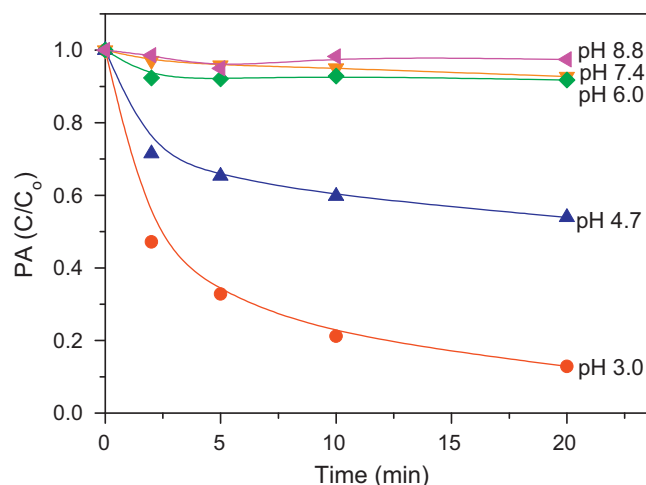**Fig. 6.** PA adsorption with PdO/CeO_2 at different pHs. Experimental conditions: $[PA]_o = 5.0 \pm 0.5$ mg L^{-1}, $T = 22\,°C$, catalyst dosage = 300 mg L^{-1}.

for PA oxidation on the catalyst surface. However, when aqueous ozone concentration was increased by two or three times, it was found that the degradation of PA in ozonation alone was only improved by 3% within 20 min. Therefore, only ozone accumulation on the catalyst surface would not necessarily lead to a significant increase in PA degradation. It is most possible that ozone was activated on the surface of PdO/CeO_2 to generate some reactive oxygen species (e.g., $^1O_2$, •O, O_2•$^-$) as suggested by the literature about the decomposition of gaseous ozone on CeO_2, alumina, etc. [25].

3.2.3. Adsorption of PA on PdO/CeO_2

According to Legube and Leitner [2], the structure of an organic molecule and its adsorption on the catalyst are critical for catalytic ozonation. With pK_a being 2.49 [26], PA mainly existed in the deprotonated form (PA$^-$) at pH 3.0–8.8 in the working solutions. As manifested in Fig. 6, the adsorbed amounts of PA on PdO/CeO_2 at pHs 3.0 and 4.7, which were both below the pH_{pzc} of the catalyst (i.e., 5.4), were obviously higher than those at pH values above 5.4. The enhanced adsorption could be attributed to the electrostatic attraction between the positively charged catalyst surface and PA$^-$. Considering the fact that PdO/CeO_2 also showed a high catalytic activity at acidic pHs, PA adsorption seemed to be critical for the catalytic ozonation.

Pd was reported to have a high complexation ability with organic compounds including carboxylates [19,20]. It is thus hypothesized that after adsorption via electrostatic attraction, PA would further complex with Pd on the catalyst surface and then become activated.

3.2.4. Effect of phosphate

Phosphate, a common ligand, has a relatively strong affinity for transition metal ions. It may negatively affect catalytic reactions by alleviating the combination between the catalyst and the reactants since tervalent anions are usually more easily adsorbed by metal oxides than divalent and monovalent anions [27–29]. The effects of phosphate (1.0 mM) on PA degradation, PA adsorption and aqueous ozone decomposition are shown in Fig. 7.

The result indicated that phosphate significantly inhibited PA degradation, leading to 14% decrease in PA removal at 20 min. However, the presence of phosphate had little effect on ozone consumption, as shown in Fig. 7B. The adsorption of PA onto the catalyst was greatly suppressed in the presence of phosphate that strongly competed for the adsorption sites against PA$^-$. Therefore, the decrease in PA removal was mainly caused by the decrease in PA adsorption onto catalyst. The effect of phosphate on
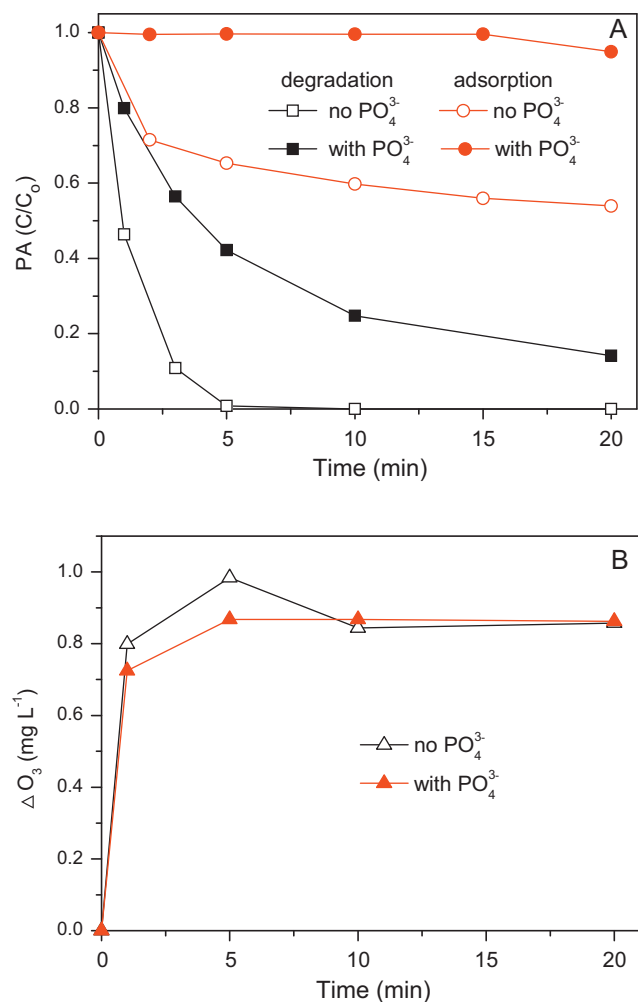
Fig. 7. Effect of phosphate (1 mM) on (A) catalytic ozonation and adsorption of PA, and (B) ozone decomposition with PdO/CeO$_2$. Experimental conditions: $[PA]_o = 5.0 \, mg \, L^{-1}$, $C_{O_3,gas} = 1.4 \, mg \, L^{-1}$, pH 6.0, $T = 22 \, ^{\circ}C$, catalyst dosage = 300 mg L^{-1}.

catalytic ozonation confirmed again that the catalysis occured on the PdO/CeO$_2$ surface and the adsorption of reactants (especially PA) onto PdO/CeO$_2$ was a critical step.

3.2.5. Active sites and possible oxygen species

In gaseous phase, ozone molecules can coordinate with weak Lewis acid sites via one of the terminal oxygen atoms [30,31], while regarding stronger Lewis acid sites, ozone decomposes after adsorption to yield a surface oxygen atom [28] or some peroxide species (e.g., $O_2^{\bullet-}$, O_2^{2-}) [32]. However, in aqueous phase, it cannot be confirmed whether the same process occurs because H$_2$O, OH$^-$ and other hard Lewis bases are commonly present. However, it has been commonly accepted that more surface Lewis acid sites result in more surface hydroxyl groups and chemisorbed water, causing a higher reactivity. In situ ATR-FTIR analysis was carried out in D$_2$O to investigate the interaction between the surface Lewis acid sites of the catalyst and water molecules (Fig. 8A). The stretching vibration of the hydrogen-bounded MeO-D (Me: Ce or Pd) was at 2557 cm^{-1}, while those of the hydrogen-bonded D$_2$O were at 2278 and 1190 cm^{-1} [21]. The peak intensities of PdO/CeO$_2$ were notably stronger than those of CeO$_2$, indicating that PdO/CeO$_2$ possessed more surface Lewis acid sites due to its adsorption of more D$_2$O. Therefore, Pd mainly accounted for the increase of Lewis acid sites on the surface of PdO/CeO$_2$.
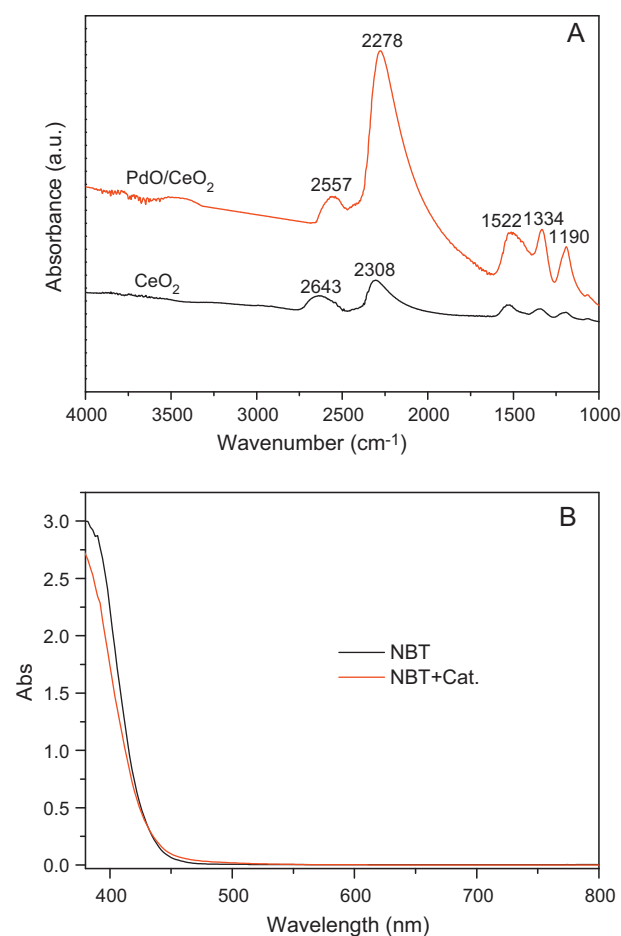

Fig. 8. (A) ATR-FTIR spectra of CeO$_2$ and PdO/CeO$_2$ suspended in D$_2$O; (B) UV–vis spectra of NBT aqueous solution after ozonation and catalytic ozonation for 10 min ($[NBT]_o = 3.0 \, mM$, $C_{O_3,gas} = 1.4 \, mg \, L^{-1}$, pH 4.7, $T = 22 \, ^{\circ}C$).

Inferred from the positive effect of *t*-BuOH on the catalytic ozonation of PA, $^{\bullet}$OH, either in water or on catalyst surface, was not the main active oxidant. According to the literature [33,34], nitro blue tetrazolium (NBT) can be applied to detect the $O_2^{\bullet-}$ species since it does not react with other active oxygen species except $^{\bullet}$OH. NBT can react with $O_2^{\bullet-}$ to form diformazan that has a characteristic absorption wavelength of 530 nm. As the effect of $^{\bullet}$OH was negligible at pH 4.7, NBT was used here to detect the $O_2^{\bullet-}$ species. The removal of NBT by catalytic ozonation could be neglected as the total decrease was measured to be less than 5% (data not shown). However, no notable difference in absorbance at 530 nm was observed after ozonation and catalytic ozonation of NBT for 10 min (Fig. 8B). Therefore, $O_2^{\bullet-}$ was not responsible for PA degradation, too.

Due to the lack of applicable detection means, other possible active species (e.g., the mostly suggested $^{\bullet}$O), could not be confirmed at present.

4. Conclusions

The degradation of PA was mainly occured on the catalyst surface at pH values below 7.4 in the catalytic ozonation with PdO/CeO$_2$. Synergetic effect was observed between CeO$_2$ and PdO on aqueous ozone decomposition and PA removal as well. The adsorption of ozone and especially PA was critical for the catalytic degradation of PA. Pd deposition on CeO$_2$ increased the surface Lewis acid sites of the catalyst and also provided main active sites for PA degradation. The $^{\bullet}$OH and $O_2^{\bullet-}$ radicals were excluded as

possible oxidation species in this study. However, other potential secondary oxidants, such as $\cdot O$ and $^1O_2$, still require further investigation.

PdO/CeO$_2$ was more effective in catalyzing the ozonation of PA at elevated pH values (i.e., 4.7–6.0) than the previously reported catalysts. Therefore, it may have a prospective application in catalytic ozonation of other organic compounds (e.g., natural organic matter) in water treatment.

Acknowledgments

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